

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
11 December 2003 (11.12.2003)

PCT

(10) International Publication Number  
**WO 03/101862 A1**

(51) International Patent Classification<sup>7</sup>: **B65D 83/00**,  
B32B 27/32, 27/38

(21) International Application Number: PCT/JP03/06799

(22) International Filing Date: 29 May 2003 (29.05.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
2002-160745 31 May 2002 (31.05.2002) JP

(71) Applicant (*for all designated States except US*): **DOW CORNING TORAY SILICONE CO., LTD.** [JP/JP]; 1-3, Marunouchi 1-chome, Chiyoda-ku, Tokyo 100-0005 (JP).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **MORIMOTO, Hirotoki** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., Science and Technology Division, 2-2, Chigusaigaan, Ichihara-shi, Chiba 299-0108 (JP). **YASUHARA, Katsuyoshi** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., Fukui Plant, 4-12-1, Yachi, Kanazu-cho, Sakai-gun, Fukui 919-0603 (JP). **HORITA, Eiji** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., Fukui Plant, 4-12-1,

Yachi, Kanazu-cho, Sakai-gun, Fukui 919-0603 (JP). **TESHIMA, Atsushi** [JP/JP]; c/o Dow Corning Toray Silicone Co., Ltd., 1-3, Marunouchi 1-chome, Chiyoda-ku, Tokyo 100-0005 (JP).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

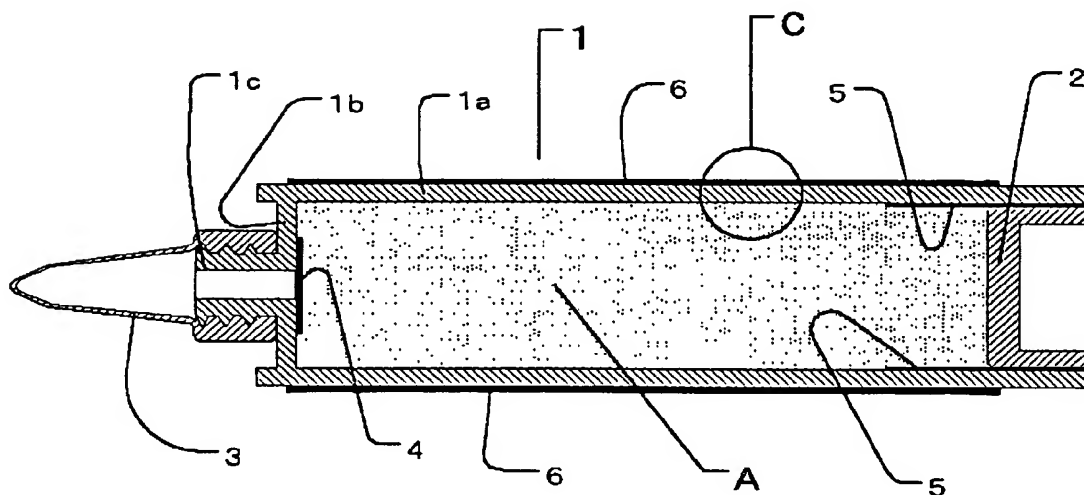
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: CARTRIDGE FOR MOISTURE-CURABLE SEALANT



(57) Abstract: A moisture-curable sealant cartridge (1) comprising a cylindrical polyolefin cartridge body (1a) having at one end thereof a polyolefin end member (1b) with an exit port and at the other end an opening sized to receive a slidably engageable extrusion plunger (2), characterized in that an electromagnetic radiation-curable epoxy compound-based composition (6) is coated and cured onto at least that portion of the cartridge body, which in use will encompass moisture-curable sealant held in the cartridge. The cartridge in accordance with the invention provides a moisture-curable sealant cartridge that exhibits an excellent moisture barrier performance and thereby enables the long-term storage of moisture-curable sealant filled therein.



WO 03/101862 A1

DESCRIPTIONCARTRIDGE FOR MOISTURE-CURABLE SEALANT

5

Technical Field

[0001] This invention relates to a cartridge for use with a moisture-curable sealant (referred to below as a moisture-curable sealant cartridge) that exhibits an improved moisture barrier performance. The invention also relates to the aforesaid cartridge filled with a moisture-curable sealant and a method for making the aforesaid cartridge.

10

Background Art

[0002] A wide range of cartridges for holding and storing moisture-curable sealants have been proposed, for example in Japanese Publication of Examined Utility Model Application Number Hei 3-28941 (28,941/1991) there is provided a cartridge in which an end member is disposed at and closes one end of a cylindrical cartridge body, a nozzle-equipped discharge member is disposed in the center of this end member, the exit port in the discharge member is sealed by a moisture-proof film, and an extrusion plunger is slidably engaged in the other end of said cartridge body.

20 [0003] The use of polyolefin resins, such as polyethylene or polypropylene, and aluminium (Al) foil-laminated thick paper (JP Kokai 2001-240154) as cartridge body materials is known. However, spent cartridges using Al foil-laminated thick paper as the cartridge body are unsuitable for disposal as industrial waste by incineration and cartridges made from polyolefin resins, such as polyethylene or polypropylene, are known to suffer from  
25 inadequate moisture barrier performance.

[0004] Depending on the particular type of moisture-curable sealant contained in the cartridge, the moisture that permeates through the cross section of the cartridge body during long-term storage can cause problems including partial curing and, in cases when the  
30 substrate to which sealant is applied e.g., glass sheet, metal sheet, or metal sash, is being maintained at a high temperature at the time of sealant application, the production of bubbles in the sealant material is likely to occur at the interface between the substrate and the sealant.

[0005] The use of inner coatings between the body of a cartridge and the outer surface of the related plunger have been described in, for example, JP Kokai S63-27584 which describes the use of a two component composition comprising:-

(i) from 90 to 10(wt)% of a wax having a melting point (m.p.) of preferably  $\geq 45^{\circ}\text{C}$ ; and

5 (ii) from 10 to 90% of polybutene or polyisobutylene

as a sealing agent for sealing between the inner peripheral surface of the cylindrical main body of a cartridge and the outer peripheral surface of a plunger slidably fit in the cylindrical main body.

10 [0006] JP Kokai Hei 11-321895 and JP Kokai Hei 11-321896 describe a synthetic-resin-made tubular container for e.g. storing cosmetics. The container is made using the following steps:-

1. A cylindrical primary molding is molded by injection molding with polyester resin-based synthetic resin.

15 2. A secondary molding having a body, a shoulder, and a neck integrally is molded from the cylindrical primary molding by biaxially orientation blow molding procedure.

3. The secondary molding is coated with an epoxy resin.

In the description of the both applications, an epoxy resin is combined with a solvent and coated by dipping, spraying or printing and cured by heating. The epoxy resin is an

20 oligomer resin, preferably a glycidyl ether or glycidyl ester type.

#### Disclosure of Invention

[0007] The object of this invention is to solve the problems identified above in the prior art by providing a moisture-curable sealant cartridge that exhibits an excellent moisture barrier  
25 performance and thereby enables the long-term storage of moisture-curable sealant contained therein.

[0008] In accordance with the present invention there is provided a moisture-curable sealant cartridge comprising a cylindrical polyolefin cartridge body having at one end  
30 thereof a polyolefin end member with an exit port and at the other end an opening sized to receive a slidably engageable extrusion plunger, characterized in that an electromagnetic radiation-curable epoxy compound-based composition is coated and cured onto at least that portion of the cartridge body, which in use will encompass moisture-curable sealant held in

the cartridge. It is preferable that the moisture-curable sealant cartridge additionally comprises a slidably engageable extrusion plunger received in the opening.

[0009] This invention additionally relates to a moisture-curable sealant cartridge filled with  
5 a moisture-curable sealant comprising the aforesaid moisture-curable sealant cartridge, a  
slidably engageable extrusion plunger received in the opening, and a moisture-curable  
sealant filled in the body of the aforesaid cartridge and to a method for producing moisture-  
curable sealant cartridge bodies characterized by coating an electromagnetic radiation-  
10 curable epoxy compound-based composition on the aforesaid cartridge body and thereafter  
curing the electromagnetic radiation-curable epoxy compound-based composition by  
exposure to radiated active energy.

[0010] The cartridge body and end member are preferably molded as a single unit made  
from a polyolefin. The extrusion plunger may be made from any suitable material such as  
15 for example a thermoplastic resin, a polyolefin or metal although the use of polyolefin is  
preferred. Any suitable polyolefin may be used, for example, high-density polyethylene,  
low-density polyethylene, polypropylene, and ethylene-propylene copolymer. High-density  
polyethylene is particularly preferred.

[0011] Any suitable method for molding the cartridge body, end member, discharge  
20 member, and extrusion plunger may be used. For example, the discharge member, end  
member, and cartridge body may be integrally molded by injection molding. Alternatively  
the end member may be made by injection molding, and the cylindrical cartridge body may  
be made by extrusion molding, and then the resulting components may be melt-bonded to  
25 each other.

[0012] Preferably the end member comprises a discharge member which forms a discharge  
channel from the exit port. The discharge member may be in the form of a nozzle or more  
preferably is releasably interengageable with a nozzle in view of the advantages this affords  
30 with regard to storage and transport of the cartridge. The discharge channel may be sealed  
prior to use but in use, once the seal has been removed or broken, is adapted to guide sealant  
being dispensed from the cartridge body into the nozzle for application onto a substrate.

[0013] The thickness of each of the cartridge body, end member, and extrusion plunger is individually preferably in the range of from 0.7 to 2.5 mm. A thickness below the lower limit of this range results in problems such as an inadequate cartridge strength and unacceptable moisture barrier performance. A thickness above the upper limit on the given  
5 range causes problems such as poor economics and a reduction in workability due to the increased weight.

[0014] A moisture proof film preferably seals the exit port of the discharge member that is disposed in the center of the end member. This moisture proof film may be of any suitable  
10 type but preferably comprises a laminate of a metal foil, such as aluminum, with a hot-melt adhesive in which case the exit port is preferably sealed by melt-bonding the hot-melt adhesive side of the moisture proof film over the inner surface of the discharge member.

[0015] In use sealing is preferably carried out by first filling the cartridge body with  
15 moisture-curable sealant and then inserting the extrusion plunger. The seals on the exit port and where present the discharge member are then broken or removed, where required a nozzle is engaged on the discharge member. Pressure is then applied on the extrusion plunger forcing sealant to travel through the exit port, discharge member and where present nozzle for application onto the target substrate.

[0016] Preferably a layer of hydrophobic sealant is provided on at least the region of the inner wall surface of the cartridge body that is in contact with the extrusion plunger. Any suitable hydrophobic sealant may be utilized such as for example long-chain alkyl-modified polysiloxane; waxes such as paraffin wax, microcrystalline wax, vegetable waxes, animal  
25 waxes, and polyethylene waxes; or a mixture of such waxes with polybutene or polyisobutylene.

[0017] The moisture-curable sealant cartridge of the type described above is already known for retaining moisture-curable sealants. However, in the present invention an  
30 electromagnetic radiation-curable epoxy compound-based composition is coated and cured on at least that portion of the cartridge body that, in use encompasses or holds moisture-curable sealant. The resulting cured coating is adapted to prevent the ingress of atmospheric moisture into the cartridge interior by preventing the permeation of atmospheric moisture

through the cartridge body. This enables long-term storage of moisture-curable sealant held therein. The electromagnetic radiation-curable epoxy compound-based composition may be coated and cured over the entire outer surface and/or the entire internal surface of the cartridge body and may also be coated over all or part of the end member. However, the  
5 electromagnetic radiation-curable epoxy compound-based composition must be coated and cured on at least that portion of the outer surface and/or internal surface of the cartridge body that encompasses or holds the moisture-curable sealant.

[0018] The electromagnetic radiation-curable epoxy compound-based composition  
10 preferably contains an epoxy compound as a base resin. A cross-linking reaction within the composition is induced by exposure to electromagnetic radiation, resulting in the formation of a cured coating. The electromagnetic radiation-curable epoxy compound-based composition is preferably a liquid at room temperature and preferably does not contain solvent. The use of one or more solvents may result in the cartridge having an inadequate  
15 moisture barrier performance. This is due to such factors as the generation of pinholes in the coating originating from solvent removal after the application step and the formation of residual microscopic bubbles in the coating, etc.

[0019] Any suitable compounds having epoxy-functional groups or epoxy resins can be  
20 used, for example, aliphatic epoxy compounds such as alicyclic epoxy-functional monomers, alicyclic epoxy resins, and polyglycidyl ether monomers from aliphatic polyhydric alcohols and their alkylene oxide adducts, as well as aromatic epoxy compounds such as aromatic epoxy-functional monomers, phenol novolac-type epoxy resins, cresol novolac-type epoxy resins, and bisphenol-type epoxy resins. These epoxy-functional monomers, epoxy  
25 oligomers and/or epoxy resins can be used individually or as mixtures as required. Similarly epoxy-functional monomers, oligomers, and/or polymers that have been modified by a radically-polymerizable functional group, such as acryl- and methacryl-modified epoxy resins, as well as various epoxy-modified monomers, oligomers, and polymers such as, for example, epoxy-modified polybutadiene and epoxy-modified acrylic and methacrylic resins  
30 may be used. Bisphenol-type epoxy resins are particularly preferred because of their adhesive properties in relation to polyolefins and because they are readily available.

[0020] The electromagnetic radiation-curable epoxy compound-based composition preferably contains, in addition to the epoxy compound as described above, photopolymerization initiators, most preferably cationic photopolymerization initiators when ultraviolet radiation is used as the electromagnetic radiation for inducing cure of the composition. Cationic photopolymerization initiators are compounds that upon exposure to, for example, ultraviolet radiation, release a substance that can initiate cationic polymerization and thereby induce crosslinking of the aforesaid epoxy compounds. The photopolymerization initiator may alternatively be a radical photopolymerization initiator. Radical photopolymerization initiators are compounds that upon exposure to, for example, ultraviolet radiation, release a substance that can initiate radical polymerization and can thereby crosslink an acrylic or methacrylic compound that contains at least one unsaturated acryloyl group. In the case of the use of a radical photopolymerization initiator, the electromagnetic radiation-curable epoxy compound-based composition may be exemplified by a composition comprising a radical photopolymerization initiator and a polymerizable monomer comprising an acrylate or methacrylate ester and a polymerizable prepolymer containing an epoxy skeleton, e.g., epoxy acrylate.

[0021] The electromagnetic radiation-curable epoxy compound-based composition used by this invention may contain other additives within a range that does not impair the object of the invention. These additives may for example include viscosity regulators, sagging inhibitors, water resistance agents, dispersants, crosslinkers, gelling agents, antiskinning agents, delustrants, defoamers, color separation inhibitors, antimolds, mist inhibitors, slip agents, antioxidants, drying agents, humectants, waxes, organic pigments, inorganic pigments, moisture-resistant pigments, carbon black, titanium white, metal powders, polymerization accelerators, and polymerization inhibitors capable of preventing the problems of polymerization in the dark and polymerization during storage.

[0022] Commercial electromagnetic radiation-curable epoxy compound-based inks, paints, and coatings are well-suited for use as the electromagnetic radiation-curable epoxy compound-based composition under consideration. For example, FDSS46 and FDSS210 from Toyo Ink Mfg. Co., Ltd., UV POL from Teikoku Printing Inks Mfg. Co., Ltd., and Series 9076 Ink from the MARKEM Corporation are well-suited for use as the electromagnetic radiation-curable epoxy compound-based composition.

[0023] These electromagnetic radiation-curable epoxy compound-based compositions adhere well to polyolefins such as high-density polyethylene, low-density polyethylene, polypropylene, and ethylene-propylene copolymers, cure rapidly, and provide cured films that exhibit excellent film strength, friction resistance, water resistance, and weathering resistance.

[0024] The electromagnetic radiation-curable epoxy compound-based compositions may be applied onto a cartridge body by any suitable method, such as for example roll coating, offset coating, gravure coating, gravure-offset coating, spray coating, immersion coating, and screen printing. Once the cartridge body has been coated with the composition, the treated cartridge body may be exposed to electromagnetic radiation over its whole surface; alternatively electromagnetic radiation may be irradiated from a single location while the cartridge body is rotated.

[0025] Ultraviolet radiation, x-rays, and electron beams are examples of the electromagnetic radiation that can be used to induce cure of the electromagnetic radiation-curable epoxy compound-based composition. A variety of light sources may be used in the case of cure induction using ultraviolet radiation, such as, for example, pressurized and high-pressure mercury lamps, ultrahigh-pressure mercury lamps, metal halide lamps, gallium lamps, xenon lamps, and carbon arc lamps. Light sources that generate light with a wavelength of 200-500 nm are preferred. The ultraviolet radiation can be used in combination with heat generated by, for example, infrared radiation, far infrared radiation, a hot gas current, or high-frequency radiation. Metal halide lamps are preferred for use as the ultraviolet source because they readily afford strong cured films with a high surface hardness. A variety of emitting devices can be used in the case of electron beam-induced cure, for example, Cockcroft-Walton machines, van de Graaf generators, and resonance transformer devices. The electron beam preferably has an energy of from 50 to 1000 eV and more preferably of from 100 to 300 eV. Ultraviolet radiation is preferred for curing the electromagnetic radiation-curable epoxy compound-based composition because ultraviolet sources are inexpensive and easy to handle.



[0026] The cured film thickness afforded by the electromagnetic radiation-curable epoxy compound-based composition should be from 0.1 to 100  $\mu\text{m}$  and is preferably from 1 to 50  $\mu\text{m}$ . The moisture barrier performance will be inadequate below the lower limit of the given range, while exceeding the upper limit on the given range can be disadvantageous from a cost standpoint.

[0027] JIS Z 0208, "Test methods for determination of the water vapor transmission rate of moisture proof packaging", or the MOCON method corresponding to this JIS method may be used to measure the moisture permeability of the cartridge body on which the electromagnetic radiation-curable epoxy compound-based composition has been coated and cured. The moisture permeability of the cartridge body measured in a 40°C/90% RH (relative humidity) ambient is preferably no greater than 0.18  $\text{g/m}^2$  per 24 hrs. When this limit is exceeded, the storage stability will in some cases be unsatisfactory depending on the type of moisture-curable sealant contained in the cartridge.

[0028] The cartridge in accordance with the present invention provides a means for the long-term storage of moisture-curable sealants, e.g., silicone sealants, modified silicone sealants, polyurethane sealants, and polysulfide sealants, by virtue of the electromagnetic radiation-curable epoxy compound-based composition coated and cured on at least that portion of the cartridge body that encompasses or holds the moisture-curable sealant. The moisture-curable silicone sealants may have an alcohol-eliminating, oxime-eliminating, amine-eliminating, ketone-eliminating, or aminoxy-eliminating silicone sealant, but a dramatically prolonged storage life can be obtained in particular when a single-package alcohol-eliminating moisture-curable silicone sealant is stored in the inventive cartridge.

#### Best Mode for Carrying Out the Invention

[0029] The present invention will now be described further based on the following examples and drawings in which :-

Figure 1 contains a lengthwise section of the moisture-curable sealant cartridge used in the examples of this invention; and

Figure 2 contains a schematic drawing of a section of region C in Figure 1, in which

- a) illustrates an example in which the electromagnetic radiation-curable epoxy compound-based composition has been coated and cured on the outer surface of the cartridge body in accordance with the present invention,
- b) illustrates an example in which the electromagnetic radiation-curable epoxy compound-based composition has been coated and cured on the internal surface of the described cartridge body, and
- c) illustrates an example in which the electromagnetic radiation-curable epoxy compound-based composition has been coated and cured on the outer surface and the internal surface of the described cartridge body.

**[0030]** In Fig. 1 there is provided a cartridge 1 having a cartridge body 1a made from a polyolefin having at one end thereof a polyolefin end member 1b. Cartridge body 1a and end member 1b are molded as a single body. A discharge member 1c is disposed in the center of end member 1b. At the other end of the cartridge body 1a is a freely slidable extrusion plunger 2 which is also made from a polyolefin based material. The thickness of the cartridge body 1a, end member 1b, and extrusion plunger 2 is in the range of from 0.7 mm to 2.5 mm. A moisture proof film 4 is provided to seal the exit port of the discharge member 1c. This moisture proof film 4 comprises an aluminium foil/hot melt adhesive laminate such that the exit port is sealed by melt-bonding the hot-melt adhesive side of the moisture proof film 4 over the perimeter of the discharge member 1c. A nozzle 3 is preferably attached on the discharge member 1c. This nozzle 3 is preferably detachable from the discharge member 1c in view of the advantages this affords with regard to storage and transport of the cartridge, but the nozzle 3 can also be integrally formed with the discharge member 1c.

**[0031]** A coating of hydrophobic sealant 5 is provided on that region of the internal surface of the cartridge body 1a in contact with the outwardly facing surface of the extrusion plunger 2.

**[0032]** An electromagnetic radiation-curable epoxy compound-based composition 6 is coated and cured on at least that portion of the cartridge body 1a that encompasses or holds the moisture-curable sealant. The cured product afforded by the electromagnetic radiation-curable epoxy compound-based composition 6 prevents the ingress of atmospheric moisture

into the cartridge interior by preventing the permeation of atmospheric moisture through the cartridge body 1a enabling long-term storage of the moisture-curable sealant A retained therein.

5 [0033] In use the application of sealant onto a substrate is preferably carried out by first filling cartridge body 1a with moisture-curable sealant and then inserting extrusion plunger 2. The seal on the exit port 4 is broken or removed and pressure is then applied on the extrusion plunger forcing the sealant to travel through the exit port, discharge member 1c and nozzle 3 for application onto the target substrate.

10

[0034] In order to demonstrate the advantageous effects of this invention, the storage stability of moisture-curable sealant filled in inventive cartridges was evaluated by investigating sealant foaming and the occurrence of cured material in sealant subjected to accelerated ageing. The moisture permeability of the cartridges was investigated at the same

15

#### [0035] Production of the cartridge bodies

Cartridge bodies 1a were produced by injection molding using a high-density polyethylene resin (density = 0.96). The wall thickness was 1.2 mm, and one end of cartridge body 1a was closed off by an end member 1b having at its center discharge member 1c. The circumference of the exit port of the discharge member 1c was sealed from the inside by the melt-bonding thereto of a moisture proof film 4 of an aluminum/hot melt adhesive-laminated film. A tapered nozzle 3 of low-density polyethylene was screwed onto the discharge member 1c. At the other end of the cartridge body 1a, a mixture of polybutene and microcrystalline wax (mixing ratio = 3 : 2) was coated over the internal surface of the opening as a hydrophobic sealant 5 for the purpose of improving the quality of the seal when the extrusion plunger was inserted and engaged. An electromagnetic radiation-curable ink was then offset coated or screen printed on that portion of the outwardly facing surface of the cartridge body 1a that would encompass the moisture-curable sealant A.

25  
30

#### [0036] Measurement of the moisture permeability

The test specimen for evaluating moisture permeability was prepared by cutting out a sample from cartridge body 1a on which the electromagnetic radiation-curable epoxy

compound based composition 6 had been coated and cured, flattening this sample into a 1.2 mm-thick sheet by means of a hot press at 120°C, and cutting the sheet into a disk with a diameter of 64 mm. Using this test specimen on which the particular electromagnetic radiation-curable epoxy compound based composition 6 had been coated and cured, the moisture permeability was measured by JIS Z 0208, "Test methods for determination of the water vapor transmission rate of moisture proof packaging", by holding for 48 hours in a 40°C/90% RH ambient.

**[0037] Preparation of the moisture-curable silicone sealant and ageing procedure**

10 An alcohol-eliminating moisture-curable silicone sealant was prepared by mixing the following to homogeneity at room temperature and degassing: 50 parts by weight dimethylhydroxysiloxy-endblocked polydimethylsiloxane (viscosity at 25°C = 17,000 mPa.s), 50 parts by weight calcium carbonate (produced by precipitation, BET specific surface area = 18 m<sup>2</sup>/g, surface treated with fatty acid), 3.0 parts by weight methyltrimethoxysilane, and 1.0 parts by weight di(isopropoxy)titanium di(ethyl acetoacetate). This silicone sealant was filled into the above-described cartridge bodies 1a. Sealing was then carried out by engaging an extrusion plunger 2 (wall thickness = 1.1 mm), produced by the injection molding of the same high-density polyethylene as used to produce the cartridge body 1a, into the opening in the cartridge body 1a. The resulting silicone sealant-filled cartridges 1 were held for 2, 4, 8, 12, 16, or 20 weeks under accelerated ageing conditions (40°C/90% RH). The tests described below were run on cartridges after each ageing period to inspect for the presence of cured material and foaming.

**[0038] Inspection for cured material**

25 The silicone sealant, after it had been held under accelerated ageing conditions for the prescribed period of time as noted above, was extruded from the cartridge 1 and was visually inspected for the occurrence of microfine cured material.

**[0039] Inspection for foaming**

30 A joint was set up by placing two strips of backup material (width x length x height = 12 mm x 50 mm x 6 mm) in parallel 12 mm apart on a glass test panel (50 mm x 50 mm x 5 mm). This glass test panel was placed in a 50°C oven and removed after 24 hours and

silicone sealant, held for the specified period of time under the conditions described above, was immediately applied into the joint and finished with a spatula. The silicone sealant was subsequently cured by standing for 7 days in a 25°C/50% RH ambient. The occurrence of bubbles between the silicone sealant and glass test panel was then investigated.

5

#### Example 1

[0040] An ultraviolet-curing epoxy compound based composition (FDSS 46 Medium from Toyo Ink Mfg. Co., Ltd.) was offset coated on the outer surface of a cartridge body followed by curing by exposure to ultraviolet radiation from a metal halide lamp (output = 80 W/cm) at a transport rate of 15 m/min. The moisture permeability of the resulting cartridge was examined, while the storage stability of the moisture-curable silicone sealant filled into the cartridge was investigated under accelerated ageing conditions. The cured film thickness was 3 µm. The results are reported in Table 1 below.

#### 15 Example 2

[0041] A cartridge was prepared by carrying out the following process twice: offset coating the outwardly facing surface of the cartridge body with an ultraviolet-curing epoxy compound based composition (FDSS 46 Medium from Toyo Ink Mfg. Co., Ltd.) followed by curing by exposure to ultraviolet radiation from a metal halide lamp (output = 80 W/cm) at a transport rate of 15 m/min. The moisture permeability of the resulting cartridge was examined as in Example 1, while the storage stability of the moisture-curable silicone sealant filled into the cartridge was investigated under accelerated ageing conditions as in Example 1. The cured film thickness was 10 µm. The results are reported in Table 1 below.

#### 25 Example 3

[0042] An ultraviolet-curing epoxy compound based composition (FDSS 46 Medium from Toyo Ink Mfg. Co., Ltd.) was screen printed on the outer surface of the cartridge body followed by curing by exposure to ultraviolet radiation from a metal halide lamp (output = 80 W/cm) at a transport rate of 15 m/min. The moisture permeability of the resulting cartridge was examined as in Example 1, while the storage stability of the moisture-curable silicone sealant filled into the cartridge was investigated under accelerated ageing conditions as in Example 1. The cured film thickness was 30 µm. The results are reported in Table 1 below.

## Example 4

[0043] An ultraviolet-curing epoxy compound based composition (FDSS 210 Medium from Toyo Ink Mfg. Co., Ltd.) was screen printed on the outer surface of the cartridge body followed by curing by exposure to ultraviolet radiation from a metal halide lamp (output = 80 W/cm) at a transport rate of 15 m/min. The moisture permeability of the resulting cartridge was examined as in Example 1, while the storage stability of the moisture-curable silicone sealant filled into the cartridge was investigated under accelerated ageing conditions as in Example 1. The cured film thickness was 20  $\mu\text{m}$ . The results are reported in Table 1 below.

## Example 5

[0044] An ultraviolet-curing epoxy compound based composition (UV POL 310 from Teikoku Printing Inks Mfg. Co., Ltd.) was screen printed on the outer surface of the cartridge body followed by curing by exposure to ultraviolet radiation from a metal halide lamp (output = 80 W/cm) at a transport rate of 15 m/min. The moisture permeability of the resulting cartridge was examined as in Example 1, while the storage stability of the moisture-curable silicone sealant filled into the cartridge was investigated under accelerated ageing conditions as in Example 1. The cured film thickness was 20  $\mu\text{m}$ . The results are reported in Table 1 below.

## Comparative Example 1

[0045] Cartridge production was carried out as in Example 1, but in this case without application of the electromagnetic radiation-curable epoxy compound based composition on the cartridge. The moisture permeability of the resulting cartridge was examined as in Example 1, while the storage stability of the moisture-curable silicone sealant filled into the cartridge was investigated under accelerated ageing conditions as in Example 1. The results are reported in Table 1 below.

Table 1.

Abbreviations used: CM = cured material  
F = foaming

	Example 1		Example 2		Example 3		Example 4		Example 5		Comp. Ex. 1	
moisture permeability g/m <sup>2</sup> per 24 hrs	0.10		0.10		0.10		0.10		0.13		0.23	
accelerated ageing test (40°C, 90% RH)	CM	F	CM	F	CM	F	CM	F	CM	F	CM	F
after 2 weeks	no	no	no	no	no	no	no	no	no	no	no	no
after 4 weeks	no	no	no	no	no	no	no	no	no	no	no	no
after 8 weeks	no	no	no	no	no	no	no	no	no	no	no	no
after 12 weeks	no	no	no	no	no	no	no	no	no	no	no	yes
after 16 weeks	no	no	no	no	no	no	no	no	no	no	yes	yes
after 20 weeks	no	no	no	no	no	no	no	yes	no	yes	yes	yes

## Example 6

[0046] An ultraviolet-curing epoxy compound-based composition (DAICURE RT-7 from Dainippon Ink And Chemicals Inc.) was offset coated on the outwardly facing surface of the cartridge body followed by curing by exposure to ultraviolet radiation from a metal halide lamp (output = 80 W/cm) at a transport rate of 15 m/min. The moisture permeability of the resulting cartridge was examined as in Example 1, while the storage stability under accelerated ageing conditions as in Example 1. The Cured film thickness was 3  $\mu$ m. The results are reported in Table 2 below. It should however be noted that in the case of Daicure RT-7 the main-component is trimethylolpropanetriacrylate and sub-component is bisphenol epoxy resin whereas the main component in the other inks used in examples 1 to 5 are bisphenol epoxy resins and as such the results in example 6 are not as good as those in examples 1 to 5.

## Comparative Example 2

[0047] A heat-curing urethane compound-based composition (SS PO Medium from Toyo Ink Mfg. Co., Ltd.) was screen printed on the outwardly facing surface of the cartridge body followed by curing by heat at a temperature of from 80 to 90° C for 5 min. The moisture permeability of the resulting cartridge was examined as in Example 1, while the storage stability under accelerated ageing conditions as in Example 1. The cured film thickness was 5  $\mu$ m. The results are reported in Table 2 below.

Table 2.

Abbreviation used:

CM = cured material

F = foaming

	Example 6		Comp. Ex.2	
moisture permeability (g/m <sup>2</sup> ·24hrs)	0.26		0.24	
accelerated ageing test (40°C, 90%RH)	CM	F	CM	F
after 2 weeks	No	No	No	No
after 4 weeks	No	No	No	No
after 8 weeks	No	No	No	No
after 12 weeks	No	No	No	Yes
after 16 weeks	No	Yes	Yes	Yes
after 20 weeks	Yes	Yes	Yes	Yes



Industrial Application

[0048] The moisture-curable sealant cartridge according to this invention is characterized by an excellent moisture barrier performance and by the fact that it enables the long-term storage of moisture-curable sealant filled therein. These characteristic features accrue because an electromagnetic radiation-curable epoxy compound-based composition is coated and cured on at least that portion of the cartridge body that encompasses or holds the moisture-curable sealant. The moisture-curable sealant-filled cartridge according to this invention, which comprises the aforesaid moisture-curable sealant cartridge filled with moisture-curable sealant, is characteristically able to provide good usability due, even after long-term storage, to the absence of foaming by the sealant and the absence of production of cured material within the cartridge. The inventive method for producing the cartridge body for application with moisture-curable sealants is characterized by coating an electromagnetic radiation-curable epoxy compound-based composition on a cylindrical polyolefin cartridge body followed by curing by exposure to radiated active energy. This method therefore enables the highly efficient and inexpensive production of the described cartridge body.

CLAIMS

1. A moisture-curable sealant cartridge (1) comprising a cylindrical polyolefin cartridge body (1a) having at one end thereof a polyolefin end member (1b) with an exit port and at the other end an opening sized to receive a slidably engageable extrusion plunger (2), characterized in that an electromagnetic radiation-curable epoxy compound-based composition (6) is coated and cured onto at least that portion of the cartridge body, which in use will encompass a moisture-curable sealant held in the cartridge.
2. A moisture-curable sealant cartridge in accordance with claim 1, characterized in that the electromagnetic radiation is ultraviolet radiation.
3. A moisture-curable sealant cartridge in accordance with claim 1 or 2, wherein the electromagnetic radiation-curable epoxy compound-based composition comprises an epoxy compound and a photopolymerization initiator.
4. A moisture-curable sealant cartridge in accordance with any preceding claim, characterized in that the electromagnetic radiation-curable epoxy compound-based composition is a solvent-free liquid at room temperature.
5. A moisture-curable sealant cartridge in accordance with any preceding claim characterized in that the moisture permeability of the cartridge body (1a) on which the electromagnetic radiation-curable epoxy compound-based composition has been coated and cured is no greater than  $0.18 \text{ g/m}^2$  per 24 hrs.
6. A moisture-curable sealant cartridge in accordance with any preceding claim, wherein the moisture-curable sealant is a silicone sealant.
7. A moisture-curable sealant cartridge in accordance with claim 6, wherein the silicone sealant is an alcohol-eliminating silicone sealant.

8. A moisture-curable sealant cartridge in accordance with any preceding claim additionally comprising a slidably engageable extrusion plunger (2) received in the opening.

5 9. A moisture-curable sealant-filled cartridge comprising a moisture-curable sealant cartridge in accordance with claim 8 and a moisture-curable sealant which is filled in the body of the moisture-curable sealant cartridge in accordance with claim 8.

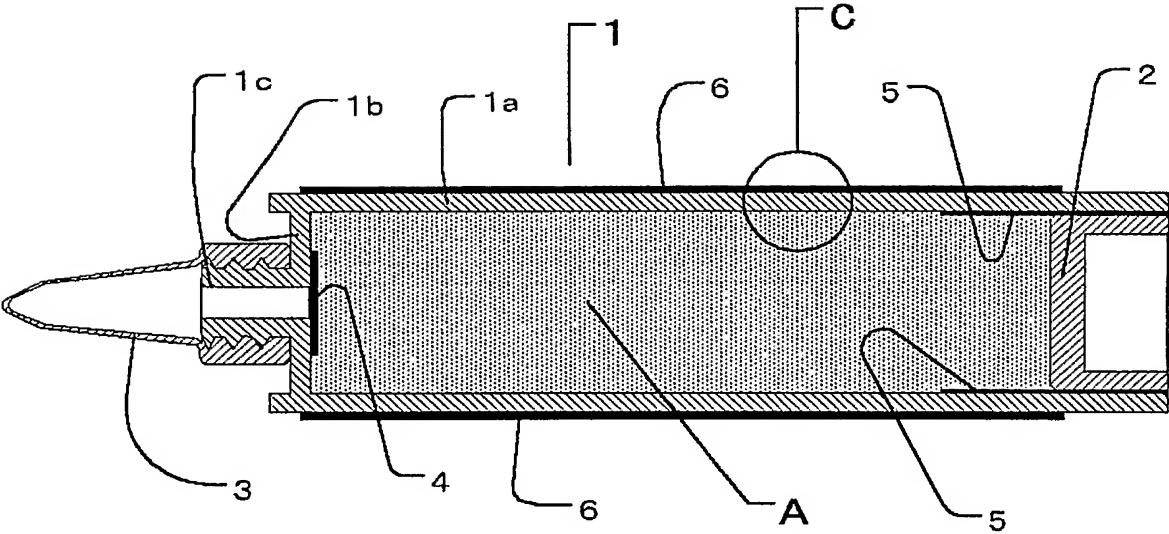
10. A moisture-curable sealant-filled cartridge in accordance with claim 9, wherein the  
10 moisture-curable sealant is a silicone sealant.

11. A method for producing a cartridge body for use with moisture-curable sealants, characterized by  
coating a cylindrical polyolefin cartridge body (1a) that is closed at one end by means  
15 of a polyolefin end member (1b) provided with an exit port and having at its other end an opening sized to receive an extrusion plunger (2) in a freely slidable manner with an electromagnetic radiation-curable epoxy compound-based composition; and curing the electromagnetic radiation-curable epoxy compound-based composition by electromagnetic radiation.

20

1/1

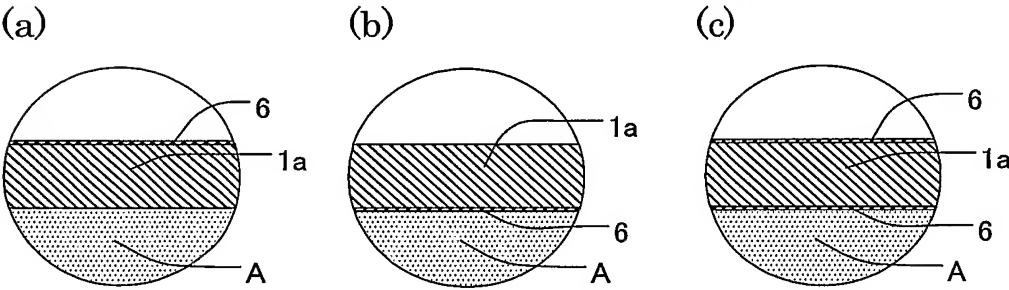
Figure 1



5

10

Figure 2



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/06799

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B65D83/00 B32B27/32 B32B27/38

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B65D B32B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 01 89722 A (HARCOSTAR DRUMS LTD) 29 November 2001 (2001-11-29) claim 1	1-11
Y	EP 1 176 105 A (DOW CORNING TORAY SILICONE) 30 January 2002 (2002-01-30) paragraph '0018!; examples 1,2	1-11
A	EP 0 327 039 A (PPG INDUSTRIES INC) 9 August 1989 (1989-08-09) claims 15-19	1-11
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### ° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

5 September 2003

Date of mailing of the international search report

22/09/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Van Nieuwenhuize, O

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/06799

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 02, 29 February 2000 (2000-02-29) & JP 11 321895 A (DAINIPPON PRINTING CO LTD), 24 November 1999 (1999-11-24) cited in the application abstract -----	1, 11
A	DE 197 13 951 A (DENTSPLY DETREY GMBH) 8 October 1998 (1998-10-08) column 2, paragraph 2 -----	1
A	DATABASE WPI Section Ch, Week 198044 Derwent Publications Ltd., London, GB; Class A17, AN 1980-78016C XP002253658 & JP 55 121057 A (HONSHU PAPER MFG CO LTD) , 17 September 1980 (1980-09-17) abstract -----	1

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 03/06799

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0189722	A	29-11-2001	AU 5854901 A	03-12-2001
			EP 1157750 A2	28-11-2001
			WO 0189722 A2	29-11-2001
			GB 2362339 A	21-11-2001
			US 2001043997 A1	22-11-2001
EP 1176105	A	30-01-2002	JP 2002037359 A	06-02-2002
			EP 1176105 A2	30-01-2002
			US 2002008123 A1	24-01-2002
EP 0327039	A	09-08-1989	CA 1337137 C	26-09-1995
			DE 68928668 D1	18-06-1998
			DE 68928668 T2	26-11-1998
			EP 0327039 A2	09-08-1989
			ES 2116261 T3	16-07-1998
			JP 2004820 A	09-01-1990
			JP 2057215 C	23-05-1996
			JP 7091368 B	04-10-1995
			MX 166278 B	28-12-1992
			MX 9205371 A1	31-03-1994
			US 5489455 A	06-02-1996
			US 5438109 A	01-08-1995
			US 5008137 A	16-04-1991
			US 5491204 A	13-02-1996
			US 5573819 A	12-11-1996
			US 5300541 A	05-04-1994
JP 11321895	A	24-11-1999	NONE	
DE 19713951	A	08-10-1998	DE 19713951 A1	08-10-1998
JP 55121057	A	17-09-1980	NONE	